

Article

Spiro Indane-Based Phosphine-Oxazolines as Highly Efficient P,N Ligands for Enantioselective Pd-Catalyzed Allylic Alkylation of Indoles and Allylic Etherification

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Abstract: A series of indane-based phosphine-oxazoline ligands with a spirocarbon stereogenic center were examined for palladium-catalyzed asymmetric allylic alkylation of indoles. Under optimized conditions, high yields (up to 98%) and enantioselectivities (up to 98% ee) were obtained with a broad scope of indole derivatives. The ligand was determined to be the most efficient P,N-ligand for this reaction. Moreover, the ligand was also efficient for Pd-catalyzed asymmetric allylic etherification with hard aliphatic alcohols as nucleophiles.

Keywords: asymmetric synthesis; indole; phosphine-oxazoline; spiro; palladium

1. Introduction

As a typical heterocyclic structural subunit, the indole scaffold is highly prevalent in biological compounds, pharmaceuticals, natural products and material science [1–5]. Notably, a variety of biologically active indole derivatives and indole-based drugs are enantiopure. Therefore, the synthesis and functionalization of chiral indole derivatives is meaningful. It is found that many 3-substituted indoles are important intermediates of natural products, such as (–)-agroclavine and (–)-aurantioclavine (Figure 1). Because of the biologically significant activities, including treatment of migraine headaches, antagonists, antiviral activity and agonist, functionalization of indoles on C-3 position has attracted much attention [6]. Enantioselective alkylation of indoles at the C-3 position by the Friedel–Crafts reaction with Lewis acid as the catalyst has been explored extensively [7–10]. However, high catalyst loading (10 %mol) is usually needed to obtain satisfactory yields and enantioselectivities.

Recently, palladium-catalyzed allylic alkylation has been proven to be an attractive strategy to achieve enantiopure 3-substituted indoles [11–14] and diligent efforts have been made to develop novel and efficient chiral palladium-complexes using the asymmetric allylic alkylation of indoles as the model reaction. Chan reported that chiral ferrocenyl P/S ligands demonstrated good catalytic performance [15]. Hoshi reported that high yields and good enantioselectivities were obtained with sulphur-MOP ligands [16]. A phosphine ligand developed by Mino afforded 89% yields and 80% enantioselectivities with narrow substrate scope [17]. Other ligands such as phosphoramidite-thioether [18], phosphoramidite-terminal olefin [19], phosphine olefin [20,21], and helicenylphosphine ligands [22] were also reported as efficient catalysts.

The P,N-ligands are an important class of ligands and have successfully been applied in a large scope of reactions because the steric and electronic characters of ligands can be finely tuned [23,24]. However, for the asymmetric allylic alkylation of indole, P,N ligands were not as effective as other ligands

mentioned above. The reaction only afforded < 10% ee using *i*Pr-phosphine-oxazoline (*i*Pr-PHOX) as the ligand [15]. Hence, design of highly active and selective P/N ligands is still desirable.

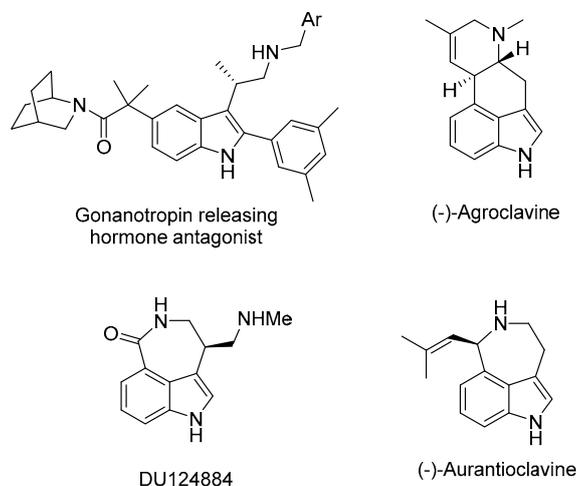
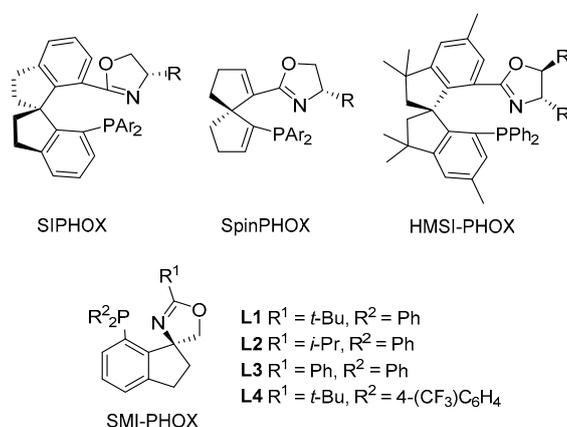


Figure 1. Selected natural products containing the indole moieties.

Spiro phosphine-oxazoline ligands exhibit impressive catalytic performance in many cases by taking advantage of the chelating units of PHOX (phosphine-oxazoline ligands) and the spiro backbone. So far, there are four kinds of spiro phosphine-oxazoline ligands reported, including SIPHOX (spirobiindane-based phosphine-oxazoline ligands) by Zhou [25–30], SpinPHOX (spiro[4.4]-1,6-nonadiene-based phosphine-oxazoline ligands) by Ding [31–34], HMSI-PHOX (hexamethyl-1,1'-spirobiindane phosphine-oxazoline ligands) by Lin [35] and SMI-PHOX (an abbreviation for spiro mono-indane-based phosphine-oxazoline ligands L1–L4 in Scheme 1) by us [36,37]. Compared with the other three ligands, SMI-PHOX ligands possess potentially distinct features: (i) first spiro indane-based phosphine-oxazoline ligand with non- C_2 -symmetric skeleton in asymmetric metal catalysis; (ii) better stability and higher rigidity; (iii) only one chiral center avoiding the complex stereochemistry; (iv) modularity by changing easily accessible carboxylic acid and $CIPR^2_2$ [36]. Because of the aforementioned properties, SMI-PHOX ligands have demonstrated excellent catalytic performance in several asymmetric reactions [36,37]. Therefore, we envisaged that they would be efficient chiral ligands for an indole C3-allylic alkylation reaction. As a result, high catalytic activities and enantioselectivities were obtained when these spiro phosphine-oxazoline ligands were used. We here disclose a detailed account of the Pd-catalyzed asymmetric allylic alkylation of indoles using a series of highly rigid spiro phosphine-oxazolines as chiral ligands.

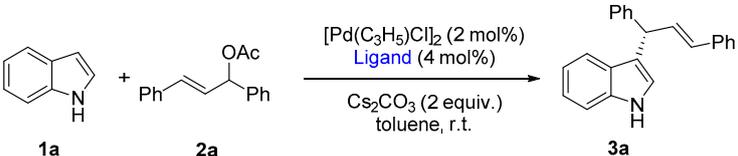


Scheme 1. Spiro-backbone-based phosphine-oxazoline ligands.

2. Results and Discussion

The chiral phosphine-oxazoline ligands **L1–L4** were synthesized according to the literature [36]. We investigated the ability of four representative spiro phosphine-oxazoline ligands **L1–L4** for palladium-catalyzed asymmetric allylic alkylation of indole. The reaction of indole (**1a**) with 1,3-diphenyl-2-propenyl acetate (**2a**) as the model reaction was examined in the presence of $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (2.0 mol%) and ligand (4.0 mol%, Pd/ligand = 1/1) in toluene at room temperature using Cs_2CO_3 (2 equivalent) as the base. The results were summarized in Table 1. The reactions gave the corresponding product **3a** in high yields (87%–95%) and enantioselectivities (87–96% ee) with the use of ligands **L1**, **L2** and **L4** (entry 1, 2, 4). However, yield and enantioselectivity slightly decreased in the presence of ligand **L3** with a phenyl substitution on the oxazoline ring (entry 3). Taking into account the catalytic activity and enantioselectivity, ligand **L1** was chosen as the optimal ligand for further intensive study.

Table 1. Evaluation of ligands for Pd-catalyzed allylic alkylation of indoles. ^a



Entry	Ligand	T (°C)	Time (h)	Yield ^b (%)	ee ^{c,d} (%)
1	L1	25	12	95	96
2	L2	25	12	87	91
3	L3	25	24	70	80
4	L4	25	12	94	87

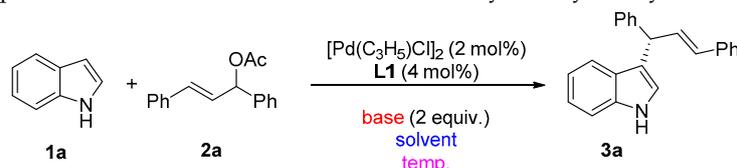
^a Unless otherwise noted, reactions were performed with **1a** (0.3 mmol), **2a** (0.36 mmol), $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (2 mol%), Ligand (4 mol%), Cs_2CO_3 (0.6 mmol) in toluene (1.5 mL) at room temperature (r.t.). ^b Isolated yield. ^c The ee values were determined by chiral high-performance liquid chromatography (HPLC) with the *N*-Boc-protected derivative of **3a**. ^d The absolute configurations were assigned as *S* via comparison of specific rotations with the literature data [20].

The reaction was investigated under various conditions using the ligand **L1**. The results are summarized in Table 2. It was shown that solvents have a great influence on the reaction activity and enantioselectivity (entries 1–8). High yield (95%) and excellent enantioselectivity (96% ee) were obtained with toluene as the solvent (entry 1). When the reaction was carried out in xylenes and mesitylene, the enantioselectivities slightly decreased (entries 2 and 3). With dichloromethane and ethyl acetate as solvents, the entioselectivities decreased to around 80% ee (entries 4 and 5). Using acetonitrile, tetrahydrofuran or *N,N*-dimethylformamide as the solvents, low yields and entioselectivities were obtained (entries 6–8). Toluene was proved to be the best choice. We next changed the base for the reaction in toluene besides of Cs_2CO_3 (entries 9 and 10). Using K_2CO_3 as the base, product **3a** was obtained with a slight decrease in enantioselectivity (89% ee) (entry 9). But the yield of **3a** decreased to 65%. With Na_2CO_3 , the enantioselectivity of the reaction dramatically decreased to 15% ee (entry 10). Subsequent optimization of temperature indicated that the reaction afforded lower yield of **3a** at 0 °C and lower enantioselectivity at 40 °C than that at room temperature (entries 11 and 12). Compared to the results shown in entry 1, a slight decrease of yields and enantioselectivities was observed by changing the ratio of indole to 1,3-diphenyl-2-propenyl acetate from 1:1.2 to 1.2:1 (entries 13 and 14). Accordingly, the optimal reaction conditions were established as follows: 2 mol% $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$, 4 mol% of ligand **L1**, 2.0 equivalents of Cs_2CO_3 in toluene at room temperature with the molar ratio of **1a** to **2a** being 1:1.2.

With the optimized conditions in hand, we examined the substrate scope with various indoles **1a–1o** and allylic acetates **2a–2e**. As shown in Table 3, the reaction exhibited high tolerance of various substituted indoles. All reactions gave high yields and enantioselectivities either with substituents

in the C2 position or in the phenyl ring. With 2-substituted indoles **1b–1c**, the reactions proceeded smoothly to obtain the desired products **3b** and **3c** with 85–89% yields and 86–96% ee. C4, C5, C6 and C7-substituted indoles **1d–1o** underwent the reactions smoothly to give the corresponding products **3d–3o** in consistently high yields (86%–98%) and enantioselectivities (83–98% ee) with either electron-donating groups (Me, MeO, BnO) or electron-withdrawing (Cl, Br) groups in the phenyl ring. The electronic properties of the substituents in the phenyl ring of the indoles have no obvious effect on the reaction. As for the 1,3-diaryllallyl acetate components, the substrates bearing either electron-donating (OMe) or electron-withdrawing (NO₂) substituents at the *para* position of the benzene ring underwent the reaction smoothly to give the corresponding products in good yield with excellent ee values (Table 3, **3p–3s**). To summarize Table 3, the ligand **L1** exhibits superior catalytic performance for allylic alkylation reaction of 1,3-diaryl-2-propenyl acetate and indoles.

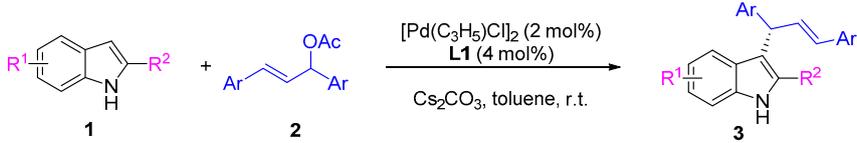
Table 2. Optimization of reaction conditions for Pd-catalyzed allylic alkylation of indoles. ^a



Entry	Solvent	Base	Time (h)	T (°C)	Yield ^b (%)	ee ^{c,d} (%)
1	toluene	Cs ₂ CO ₃	12	25	95	96
2	xylenes	Cs ₂ CO ₃	12	25	86	94
3	mesitylene	Cs ₂ CO ₃	12	25	84	90
4	CH ₂ Cl ₂	Cs ₂ CO ₃	12	25	76	83
5	EtOAc	Cs ₂ CO ₃	12	25	74	84
6	CH ₃ CN	Cs ₂ CO ₃	24	25	47	19
7	THF	Cs ₂ CO ₃	24	25	49	3
8	DMF	Cs ₂ CO ₃	48	25	N.R. ^e	N.D. ^f
9	toluene	K ₂ CO ₃	12	25	65	89
10	toluene	Na ₂ CO ₃	12	25	76	15
11	toluene	Cs ₂ CO ₃	12	0	70	90
12	toluene	Cs ₂ CO ₃	12	40	84	79
13 ^g	toluene	Cs ₂ CO ₃	12	25	91	94
14 ^h	toluene	Cs ₂ CO ₃	12	25	90	95

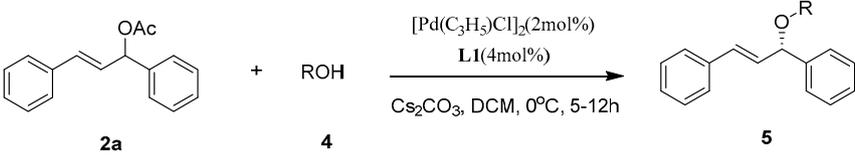
^a Unless otherwise noted, reactions were performed with **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd(C₃H₅)Cl]₂ (2 mol%), **L1** (4 mol%), base (0.6 mmol) in solvent (1.5 mL) at a certain temperature. ^b Isolated yield. ^c The ee values were determined by chiral HPLC with the *N*-Boc-protected derivative of **3a**. ^d The absolute configurations were assigned as *S* via comparison of specific rotations with the literature data [20]. ^e No reaction. ^f Not detected. ^g The molar ratio of **1a** to **2a** was 1:1. ^h The molar ratio of **1a** to **1b** was 1.2:1.

Encouraged by the excellent results achieved in the asymmetric allylic alkylation of indole, we successfully extended the current catalytic system to Pd-catalyzed asymmetric allylic etherification [38–41] by directly utilizing relatively hard aliphatic alcohols as nucleophiles (Table 4). We were pleased to find that the protocol is applicable to aromatic rings of benzylic alcohols with different electronic and steric natures. For example, a wide variety of benzylic alcohols bearing electron-donating (MeO) or electron-withdrawing (Br) groups at *ortho*-, *meta*-, or *para*-positions were well tolerated, and afforded the corresponding products **5a–5e** in consistently high yields and enantioselectivities with dichloromethane (DCM) as the solvent (Table S1). When the aryl group was changed to naphthyl and aromatic heterocycle, good yields and ee values were also observed (**5f** and **5g**). Notably, spiro phosphine-oxazoline ligand **L1** also worked efficiency in the asymmetric allylic etherification of simple aliphatic alcohols, including primary and secondary alcohols, which led to the formation of the desired products in excellent enantioselectivities (**5h–5j**, 93–99% ee).

Table 3. Substrate scope of asymmetric allylic alkylation of indoles. ^a


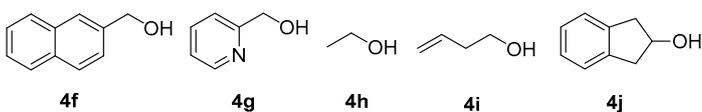
Entry	R ¹	R ²	Ar	Product	Yield ^b (%)	Ee ^{c,d} (%)
1	H	H	Ph	3a	95	96
2	H	Me	Ph	3b	89	96
3	H	Ph	Ph	3c	85	86
4	4-Me	H	Ph	3d	93	84
5	4-MeO	H	Ph	3e	95	92
6	5-Me	H	Ph	3f	96	95
7	5-MeO	H	Ph	3g	98	98
8	5-BnO	H	Ph	3h	97	96
9	5-Cl	H	Ph	3i	95	92
10	5-Br	H	Ph	3j	92	93
11	6-Me	H	Ph	3k	90	93
12	6-Cl	H	Ph	3l	94	93
13	7-Me	H	Ph	3m	90	83
14	7-MeO	H	Ph	3n	86	84
15	7-Cl	H	Ph	3o	90	94
16	H	H	4-MePh	3p	92	94
17	H	H	4-MeOPh	3q	85	90
18	H	H	4-ClPh	3r	91	95
19	H	H	4-NO ₂ Ph	3s	87	97

^a Unless otherwise noted, reactions were performed with **1** (0.3 mmol), **2** (0.36 mmol), [Pd(C₃H₅)Cl]₂ (2 mol%), **L1** (4 mol%), Cs₂CO₃ (0.6 mmol) in toluene (1.5 mL) at room temperature. ^b Isolated yield. ^c The ee values were determined by chiral HPLC with the *N*-Boc-protected derivative of **3**. ^d The absolute configurations were assigned as *S* via comparison of specific rotations with the literature data [20].

Table 4. Substrate scope of asymmetric allylic etherification. ^a


Ar-CH₂-OH

4a: Ar = Ph
4b: Ar = 4-MeOPh
4c: Ar = 4-Br
4d: Ar = 3-Br
4e: Ar = 2-Br



Entry	4	Product	Yield ^b (%)	ee ^{c,d} (%)
1	4a	5a	99	98
2	4b	5b	97	97
3	4c	5c	93	91
4	4d	5d	95	94
5	4e	5e	93	93
6	4f	5f	97	94
7	4g	5g	86	94
8	4h	5h	98	99
9	4i	5i	97	95
10	4j	5j	96	93

^a Unless otherwise noted, reactions were performed with **2a** (0.3 mmol), **4** (0.9 mmol), [Pd(C₃H₅)Cl]₂ (2 mol%), **L1** (4 mol%), Cs₂CO₃ (0.9 mmol) in DCM (2 mL) at 0°C. ^b Isolated yield. ^c Determined by HPLC using a chiral column. ^d The absolute configurations were assigned as *S* via comparison of specific rotations with the literature data [42].

3. Materials and Methods

3.1. General Information

All solvents were purified and dried according to standard methods prior to use. All air and moisture sensitive manipulations were carried out with standard Schlenk techniques under argon. Commercially available reagents were used without further purification. Melting points were recorded on a RY-1 microscopic melting apparatus and uncorrected. ^1H - and ^{13}C -nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 spectrometer (Bruker, Rheinstetten, Germany). Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). High resolution mass spectrometry (HRMS) were performed on an Ultima Global spectrometer (Waters, Milford, MA, USA) with an electrospray ionization (ESI) source. HPLC was performed on a Shimadzu LC-20 Liquid Chromatograph (Shimadzu, Kyoto, Japan) using chiralcel OD-H, AD-H and OJ-H columns. Ligands **L1–L4** were prepared according to the reported procedure [36].

3.2. General Procedure for the Pd-Catalyzed Asymmetric Allylic Alkylation of Indoles

Ligand **L1** (5.0 mg, 4 mol%) and $[\text{Pd}(\text{C}_3\text{H}_5\text{Cl})_2]$ (2.2 mg, 2 mol%) were dissolved in toluene (1.0 mL) in a Schlenk tube under Ar. After 0.5 h of stirring at room temperature, allylic acetate **2** (0.36 mmol) dissolved in toluene (0.5 mL) was added, followed by indole **1** (0.3 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol). The mixture was stirred at room temperature for 12 h and then was diluted with CH_2Cl_2 and washed with saturated NH_4Cl (aq). The organic layers were dried over MgSO_4 and filtered, and the solvents were evaporated in vacuo. The residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the corresponding product **3**.

(*S,E*)-3-(1,3-diphenylallyl)-1H-indole (**3a**) [15]: Yellow solid (m.p. 121–123 °C), 95% yield. ^1H -NMR (500 MHz, CDCl_3) δ 7.98 (brs, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39–7.19 (m, 12H), 7.04 (t, 7.4 Hz, 1H), 6.91 (s, 1H), 6.76 (dd, J = 15.8, 7.4 Hz, 1H), 6.47 (d, J = 15.8 Hz, 1H), 5.14 (d, J = 7.4 Hz, 1H); ^{13}C -NMR (125 MHz, CDCl_3) δ 143.3, 137.4, 136.6, 132.5, 130.5, 128.4, 128.3, 127.1, 126.7, 126.3, 126.2, 122.5, 122.0, 119.8, 119.3, 118.6, 111.0, 46.1.

(*S,E*)-3-(1,3-diphenylallyl)-2-methyl-1H-indole (**3b**) [15]: Yellow solid (m.p. 39–41 °C), 89% yield. ^1H -NMR (500 MHz, CDCl_3) δ 7.83 (brs, 1H), 7.40–7.36 (m, 5H), 7.31–7.28 (m, 5H), 7.23–7.21 (m, 2H), 7.12 (t, J = 7.3 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.88 (dd, J = 15.8, 7.2 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H), 5.17 (d, J = 7.2 Hz, 1H), 2.40 (s, 3H); ^{13}C -NMR (125 MHz, CDCl_3) δ 143.4, 137.5, 135.3, 132.1, 131.6, 130.5, 128.4, 128.3, 128.2, 127.9, 127.0, 126.2, 126.1, 120.9, 119.4, 119.2, 112.8, 110.2, 45.0, 12.4.

(*S,E*)-3-(1,3-diphenylallyl)-2-phenyl-1H-indole (**3c**) [15]: Yellow solid (m.p. 40–42 °C), 85% yield. ^1H -NMR (500 MHz, CDCl_3) δ 8.09 (brs, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.45–7.31 (m, 9H), 7.26–7.24 (m, 4H), 7.19–7.14 (m, 3H), 6.99 (t, J = 7.6 Hz, 1H), 6.90 (dd, J = 15.8, 7.3 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 5.27 (d, J = 8.4 Hz, 1H); ^{13}C -NMR (125 MHz, CDCl_3) δ 143.4, 137.4, 136.2, 135.5, 132.9, 132.2, 131.0, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.0, 126.2, 126.0, 122.0, 121.1, 119.6, 113.8, 110.8, 45.1.

(*S,E*)-3-(1,3-diphenylallyl)-4-methyl-1H-indole (**3d**) [17]: White solid (m.p. 172–174 °C), 93% yield. ^1H -NMR (500 MHz, CDCl_3) δ 8.00 (brs, 1H), 7.35 (d, J = 7.4 Hz, 2H), 7.32–7.26 (m, 6H), 7.25–7.18 (m, 3H), 7.07 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 6.75 (dd, J = 15.8, 6.6 Hz, 1H), 6.25 (d, J = 15.8 Hz, 1H), 5.46 (d, J = 6.4 Hz, 1H), 2.53 (s, 3H); ^{13}C -NMR (125 MHz, CDCl_3) δ 144.1, 137.6, 137.1, 134.0, 131.2, 130.8, 129.0, 128.6, 127.2, 126.4, 125.7, 123.6, 122.3, 121.4, 119.1, 109.1, 46.6, 20.5.

(*S,E*)-3-(1,3-diphenylallyl)-4-methoxy-1H-indole (**3e**): Yellow oil, 95% yield. ^1H -NMR (500 MHz, CDCl_3) δ 7.96 (brs, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.31–7.25 (m, 6H), 7.19–7.16 (m, 2H), 7.07 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.83 (d, J = 1.8 Hz, 1H), 6.77 (dd, J = 15.8, 7.2 Hz, 1H), 6.45 (d, J = 7.8 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 5.55 (d, J = 7.2 Hz, 1H), 3.73 (s, 3H); ^{13}C -NMR (125 MHz, CDCl_3) δ 154.8, 144.7, 138.1, 137.9, 134.0, 129.9, 128.5, 128.4, 128.0, 126.8, 126.2, 125.7, 122.9, 121.1, 119.3, 117.0, 104.3, 100.0, 55.0, 46.3. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{NNaO}$ [$\text{M} + \text{Na}$] $^+$: 362.1515, found 362.1510.

(*S,E*)-3-(1,3-diphenylallyl)-5-methyl-1*H*-indole (**3f**) [15]: White solid (m.p. 113–114 °C), 96% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.90 (brs, 1H), 7.38–7.26 (m, 8H), 7.25–7.19 (m, 4H), 7.01 (d, 8.2 Hz, 1H), 6.86 (s, 1H), 6.73 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H), 2.38 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 143.6, 137.7, 135.0, 132.8, 130.6, 128.6, 127.2, 126.4, 123.8, 122.9, 119.5, 118.2, 110.9, 46.1, 21.6.

(*S,E*)-3-(1,3-diphenylallyl)-5-methoxy-1*H*-indole (**3g**) [15]: Colorless oil, 98% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.90 (brs, 1H), 7.38–7.19 (m, 11H), 6.89–6.83 (m, 3H), 6.74 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 5.09 (d, *J* = 7.3 Hz, 1H), 3.72 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 154.0, 143.5, 137.7, 132.7, 132.0, 130.8, 128.7, 128.6, 127.4, 127.3, 126.6, 126.5, 123.6, 118.6, 112.4, 111.9, 102.0, 56.0, 46.4.

(*S,E*)-5-(benzyloxy)-3-(1,3-diphenylallyl)-1*H*-indole (**3h**) [15]: Colorless oil, 97% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.82 (brs, 1H), 7.37–7.17 (m, 16H), 6.92–6.88 (m, 2H), 6.82 (s, 1H), 6.70 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.04 (d, *J* = 7.3 Hz, 1H), 4.93 (s, 2H); ¹³C-NMR (125 MHz, CDCl₃) δ 152.9, 143.3, 137.6, 137.5, 132.4, 131.9, 130.5, 128.5, 127.7, 127.6, 127.2, 126.4, 126.3, 123.5, 118.3, 112.9, 111.8, 103.4, 70.8, 46.2.

(*S,E*)-5-chloro-3-(1,3-diphenylallyl)-1*H*-indole (**3i**) [15]: Yellow oil, 95% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.01 (brs, 1H), 7.38–7.20 (m, 12H), 7.13–7.11 (m, 1H), 6.94 (s, 1H), 6.69 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.07 (d, *J* = 7.3 Hz, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 143.0, 137.4, 135.0, 132.1, 130.9, 128.6, 128.5, 128.0, 127.3, 126.6, 126.4, 125.2, 124.0, 122.5, 119.3, 118.6, 112.2, 46.0.

(*S,E*)-5-bromo-3-(1,3-diphenylallyl)-1*H*-indole (**3j**) [15]: Colorless oil, 92% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.00 (brs, 1H), 7.53 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.32–7.28 (m, 5H), 7.26–7.19 (m, 5H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.69 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 142.8, 137.2, 135.2, 132.0, 130.7, 128.4, 128.3, 127.2, 126.5, 126.3, 125.0, 123.8, 122.2, 118.4, 112.7, 112.5, 45.8.

(*S,E*)-3-(1,3-diphenylallyl)-6-methyl-1*H*-indole (**3k**) [20]: Yellow oil, 90% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.85 (brs, 1H), 7.37–7.17 (m, 11H), 7.14 (s, 1H), 6.86–6.83 (m, 2H), 6.74 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.09 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 143.4, 137.5, 137.1, 132.6, 131.8, 130.4, 128.4, 128.3, 127.1, 126.3, 124.6, 121.9, 121.1, 119.5, 118.4, 111.0, 46.2, 21.6.

(*S,E*)-6-chloro-3-(1,3-diphenylallyl)-1*H*-indole (**3l**) [20]: Yellow oil, 94% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.01 (brs, 1H), 7.38–7.28 (m, 10H), 7.26–7.20 (m, 2H), 7.00 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.72 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.09 (d, *J* = 7.4 Hz, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 143.0, 137.2, 137.0, 132.1, 130.8, 128.5, 128.4, 128.0, 127.3, 126.6, 126.3, 125.4, 123.3, 120.8, 120.2, 118.9, 111.1, 46.1.

(*S,E*)-3-(1,3-diphenylallyl)-7-methyl-1*H*-indole (**3m**) [19]: Yellow oil, 90% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.89 (brs, 1H), 7.41–7.30 (m, 9H), 7.28–7.22 (m, 2H), 7.03–6.98 (m, 2H), 6.92 (s, 1H), 6.78 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 2.50 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 143.4, 137.5, 136.2, 132.5, 130.5, 128.4, 128.3, 127.1, 126.3, 122.6, 122.3, 120.2, 119.6, 119.1, 117.6, 46.2, 16.5.

(*S,E*)-3-(1,3-diphenylallyl)-7-methoxy-1*H*-indole (**3n**): Yellow oil, 86% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.21 (brs, 1H), 7.37–7.17 (m, 10H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.95–6.88 (m, 2H), 6.74 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.10 (d, *J* = 7.4 Hz, 1H), 3.94 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 146.1, 143.5, 137.5, 132.6, 130.5, 128.4, 128.2, 127.1, 122.2, 119.8, 119.1, 112.7, 101.9, 55.3, 46.3. HRMS (ESI): calcd for C₂₄H₂₁NNaO [M+Na]⁺: 362.1515, found 362.1516.

(*S,E*)-7-chloro-3-(1,3-diphenylallyl)-1*H*-indole (**3o**): Yellow solid (m.p. 81–82 °C), 90% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.23 (brs, 1H), 7.38–7.28 (m, 9H), 7.24–7.17 (m, 3H), 6.98–6.94 (m, 2H), 6.73 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.11 (d, *J* = 7.3 Hz, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 143.0, 137.3, 133.9, 132.1, 130.9, 128.5, 128.4, 128.3, 127.3, 126.6, 126.4, 123.3, 121.5, 120.3, 119.9, 118.6, 116.6, 46.2. HRMS (ESI): calcd for C₂₃H₁₈ClNNa [M + Na]⁺: 366.1020, found 366.1018.

(*S,E*)-3-(1,3-di-*p*-tolylallyl)-1*H*-indole (**3p**) [19]: Yellow oil, 92% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.97 (brs, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.28–7.02 (m, 10H), 6.91 (s, 1H), 6.70 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.09 (d, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 140.7, 137.0, 136.8, 136.0, 135.0, 132.0, 130.4, 129.4, 129.3, 128.6, 127.0, 126.4, 122.8, 122.2, 120.1, 119.6, 119.2, 111.3, 46.0, 21.3.

(*S,E*)-3-(1,3-bis(4-methoxyphenyl)allyl)-1*H*-indole (**3q**) [43]: Yellow oil, 85% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.98 (s, 1H), 7.43–7.28 (m, 4H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 6.85–6.81 (m, 4H), 6.56 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H), 3.78 (s, 6H); ¹³C-NMR (125 MHz, CDCl₃) δ 158.9, 158.1, 136.7, 135.8, 130.8, 130.4, 129.7, 129.5, 127.5, 126.9, 122.6, 122.0, 120.0, 119.4, 119.2, 113.9, 113.8, 111.2, 55.3, 55.2, 45.4.

(*S,E*)-3-(1,3-bis(4-chlorophenyl)allyl)-1*H*-indole (**3r**) [19]: Yellow oil, 91% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.05 (brs, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.30–7.19 (m, 9H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 6.69 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 141.8, 136.9, 135.9, 133.1, 132.8, 132.4, 130.0, 129.9, 128.9, 128.8, 127.7, 126.7, 122.8, 122.5, 119.9, 119.8, 118.2, 111.4, 45.7.

(*S,E*)-3-(1,3-bis(4-nitrophenyl)allyl)-1*H*-indole (**3s**): Yellow oil, 87% yield. ¹H-NMR (500 MHz, CDCl₃) δ 8.23–8.11 (m, 5H), 7.50–7.32 (m, 6H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.90 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.5 (d, *J* = 15.8 Hz, 1H), 5.28 (d, *J* = 8.0 Hz, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.2, 146.8, 143.4, 136.7, 135.7, 130.0, 129.4, 127.0, 126.2, 124.0, 123.9, 122.8, 122.7, 119.9, 119.2, 116.2, 111.6, 46.1. HRMS (ESI): calcd for C₂₃H₁₇N₃NaO₄ [M + Na]⁺: 422.1111, found 422.1110.

3.3. General Procedure for the *N*-Boc Protection of Alkylated Indoles

To a solution of **3** (0.15 mmol) and DMAP (0.9 mg, 0.0075 mmol) in CH₂Cl₂ (3 mL) was added (Boc)₂O (49 mg, 0.225 mmol), and the solution was stirred for 0.5 h at room temperature. The resulting mixture was evaporated under reduced pressure and purified by flash column chromatography (elution with *n*-hexane/EtOAc = 30:1) to afford the *N*-Boc-protected alkylated indole (**Boc-3**).

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-1*H*-indole-1-carboxylate (**Boc-3a**) [15]: Colorless oil. 99% yield and 96% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.4 mL/min, 25 °C, UV 254 nm), Retention times: *t*_r = 13.2 min for (*S*)-isomer (major), *t*_r = 16.0 min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.12 (brs, 1H), 7.39–7.21 (m, 13H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.72 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 1.68 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.0, 142.1, 137.3, 135.8, 131.4, 131.3, 129.9, 128.6, 128.5, 128.4, 127.4, 126.8, 126.4, 124.4, 123.8, 123.1, 122.5, 120.2, 115.3, 83.7, 46.0, 28.3.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-2-methyl-1*H*-indole-1-carboxylate (**Boc-3b**) [15]: Colorless oil. 99% yield and 96% ee, determined by chiral HPLC analysis (Chiralcel OJ-H hexane/isopropanol, 99:1 *v/v*, 0.3 mL/min, 25 °C, UV 254 nm), Retention times: *t*_r = 37.2 min for (*R*)-isomer (minor), *t*_r = 50.1 min for (*S*)-isomer (major). ¹H-NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.34–7.27 (m, 7H), 7.23–7.19 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.20 (d, *J* = 7.4 Hz, 1H), 2.62 (s, 3H), 1.70 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.7, 142.3, 137.2, 136.0, 134.0, 131.5, 130.5, 128.9, 128.5, 128.3, 128.0, 127.2, 126.3, 123.1, 122.2, 119.5, 119.1, 115.3, 83.6, 44.5, 28.3, 14.3.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-2-phenyl-1*H*-indole-1-carboxylate (**Boc-3c**) [15]: White solid (m.p. 153–155 °C). 98% yield and 86% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 99:1 *v/v*, 0.8 mL/min, 25 °C, UV 254 nm), Retention times: *t*_r = 5.1 min for (*S*)-isomer (major), *t*_r = 13.4 min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.29 (d, *J* = 8.6 Hz, 1H), 7.42–7.36 (m, 5H), 7.33–7.17 (m, 12H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.77 (dd, *J* = 15.8, 7.6 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 4.85 (d, *J* = 7.6 Hz, 1H), 1.22 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.4, 142.8,

137.6, 137.2, 136.9, 134.5, 131.9, 130.9, 130.3, 128.7, 128.5, 128.4, 128.2, 128.1, 127.5, 126.6, 124.5, 122.8, 121.5, 121.2, 115.6, 83.3, 45.1, 27.8.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-4-methyl-1*H*-indole-1-carboxylate (**Boc-3d**) [18]: White solid (m.p. 137–139 °C). 98% yield and 84% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 7.1$ min for (*S*)-isomer (major), $t_r = 8.5$ min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.07 (brs, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.35–7.25 (m, 8H), 7.24–7.19 (m, 2H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.73 (dd, *J* = 15.8, 6.6 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 5.37 (d, *J* = 6.6 Hz, 1H), 2.50 (s, 3H), 1.68 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 149.9, 142.8, 137.4, 136.4, 132.7, 131.3, 131.2, 128.9, 128.6, 127.4, 126.7, 126.5, 125.0, 124.9, 124.4, 123.5, 113.2, 83.7, 46.6, 28.3, 27.5, 20.4.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-4-methoxy-1*H*-indole-1-carboxylate (**Boc-3e**): Colorless oil. 99% yield and 92% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 7.8$ min for (*S*)-isomer (major), $t_r = 11.6$ min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 7.73 (brs, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.30–7.27 (m, 7H), 7.20 (t, *J* = 7.8 Hz, 3H), 6.73 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.46 (d, *J* = 7.4 Hz, 1H), 3.70 (s, 3H), 1.66 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 154.3, 150.0, 143.5, 137.7, 137.3, 132.9, 130.5, 128.5, 128.2, 127.1, 126.4, 126.1, 125.3, 123.4, 122.6, 119.6, 108.3, 103.8, 93.7, 55.2, 46.5, 28.3. HRMS (ESI): calcd for C₂₉H₂₉NNaO₃ [M + Na]⁺: 462.2040, found 462.2033.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-5-methyl-1*H*-indole-1-carboxylate (**Boc-3f**) [15]: White solid (m.p. 151–152 °C). 98% yield and 95% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, ultraviolet (UV) 254 nm), Retention times: $t_r = 7.5$ min for (*S*)-isomer (major), $t_r = 8.9$ min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 7.96 (brs, 1H), 7.37–7.27 (m, 9H), 7.25–7.19 (m, 2H), 7.12–7.09 (m, 2H), 6.68 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H), 2.35 (s, 3H), 1.65 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.0, 142.2, 137.3, 134.0, 131.9, 131.4, 131.3, 130.1, 128.6, 128.5, 127.4, 126.7, 126.4, 125.8, 123.9, 122.8, 119.9, 114.9, 83.5, 45.9, 28.3, 21.5.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-5-methoxy-1*H*-indole-1-carboxylate (**Boc-3g**) [15]: Yellow oil. 98% yield and 98% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 8.0$ min for (*S*)-isomer (major), $t_r = 10.2$ min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 7.99 (brs, 1H), 7.39–7.22 (m, 11H), 6.91 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.69 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 5.00 (d, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 1.67 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 155.8, 155.0, 142.2, 137.4, 131.5, 131.3, 130.9, 128.8, 128.7, 128.6, 127.6, 126.9, 126.6, 124.7, 123.0, 116.1, 112.9, 103.3, 83.7, 55.8, 46.2, 28.4, 27.6.

(*S,E*)-*tert*-butyl 5-(benzyloxy)-3-(1,3-diphenylallyl)-1*H*-indole-1-carboxylate (**Boc-3h**) [15]: Colorless oil. 99% yield and 96% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.35 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 34.3$ min for (*S*)-isomer (major), $t_r = 38.3$ min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.00 (brs, 1H), 7.38–7.30 (m, 13H), 7.28–7.22 (m, 3H), 6.99 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.69 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 4.98 (d, *J* = 5.0 Hz, 3H), 1.67 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 154.9, 150.0, 142.2, 137.4, 131.5, 131.3, 130.9, 128.8, 128.7, 128.6, 128.0, 127.7, 127.6, 126.9, 126.6, 124.7, 123.0, 116.2, 113.9, 104.7, 83.7, 70.8, 46.2, 28.4.

(*S,E*)-*tert*-butyl 5-chloro-3-(1,3-diphenylallyl)-1*H*-indole-1-carboxylate (**Boc-3i**) [15]: White solid (m.p. 54–56 °C). 99% yield and 92% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 8.2$ min for (*S*)-isomer (major), $t_r = 9.0$ min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.02 (brs, 1H), 7.37–7.27 (m, 10H), 7.24–7.20 (m, 2H), 6.64 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H),

4.98 (d, $J = 7.3$ Hz, 1H), 1.65 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3) δ 149.6, 141.7, 137.1, 134.2, 131.6, 131.1, 130.8, 128.7, 128.6, 128.4, 128.2, 127.5, 127.0, 126.4, 125.1, 124.6, 122.5, 119.6, 116.4, 84.2, 45.8, 28.2.

(*S,E*)-*tert*-butyl 5-bromo-3-(1,3-diphenylallyl)-1*H*-indole-1-carboxylate (**Boc-3j**) [15]: White solid (m.p. 72–73 °C). 96% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 8.2$ min for (*S*)-isomer (major), $t_r = 8.8$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.99 (brs, 1H), 7.46 (s, 1H), 7.38–7.36 (m, 4H), 7.33–7.27 (m, 6H), 7.26–7.21 (m, 2H), 6.67 (dd, $J = 15.8, 7.3$ Hz, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 4.99 (d, $J = 7.3$ Hz, 1H), 1.65 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3) δ 149.4, 141.5, 137.0, 134.5, 131.5, 131.4, 130.7, 128.6, 128.4, 128.2, 127.4, 127.2, 126.8, 126.3, 124.8, 122.5, 122.3, 116.6, 115.8, 84.1, 45.6, 28.1.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-6-methyl-1*H*-indole-1-carboxylate (**Boc-3k**): White solid (m.p. 121–123 °C). 99% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 7.2$ min for (*S*)-isomer (major), $t_r = 8.2$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.97 (brs, 1H), 7.37–7.18 (m, 12H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.69 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.44 (d, $J = 15.8$ Hz, 1H), 5.01 (d, $J = 7.4$ Hz, 1H), 2.44 (s, 3H), 1.65 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3) δ 150.0, 142.2, 137.3, 136.3, 134.4, 131.3, 131.2, 128.6, 128.5, 128.4, 127.6, 127.4, 126.7, 126.4, 123.9, 123.1, 123.0, 119.7, 115.6, 83.5, 46.0, 28.2, 22.0. HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_2$ [$\text{M} + \text{Na}$] $^+$: 446.2091, found 446.2093.

(*S,E*)-*tert*-butyl 6-chloro-3-(1,3-diphenylallyl)-1*H*-indole-1-carboxylate (**Boc-3l**): Colorless oil. 98% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 8.5$ min for (*S*)-isomer (major), $t_r = 9.2$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 8.14 (brs, 1H), 7.36–7.19 (m, 12H), 7.10 (dd, $J = 8.3, 1.7$ Hz, 1H), 6.67 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 5.00 (d, $J = 7.3$ Hz, 1H), 1.66 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3) δ 171.2, 149.5, 141.8, 137.1, 136.2, 131.5, 130.9, 130.4, 128.7, 128.6, 128.4, 127.5, 126.9, 126.4, 124.3, 123.0, 122.9, 120.9, 115.6, 84.3, 60.4, 45.9, 28.2, 21.1, 14.2. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{26}\text{ClNNaO}_2$ [$\text{M} + \text{Na}$] $^+$: 466.1544, found 466.1547.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-7-methyl-1*H*-indole-1-carboxylate (**Boc-3m**) [19]: White solid (m.p. 123–124 °C). 99% yield and 83% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 7.6$ min for (*S*)-isomer (major), $t_r = 8.9$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.39–7.28 (m, 9H), 7.26–7.18 (m, 3H), 7.09–7.04 (m, 2H), 6.71 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.45 (d, $J = 15.8$ Hz, 1H), 5.03 (d, $J = 7.4$ Hz, 1H), 2.64 (s, 3H), 1.63 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3) δ 149.6, 142.0, 137.2, 135.4, 131.2, 131.1, 131.0, 128.4, 128.3, 127.6, 127.2, 126.5, 126.3, 125.9, 125.3, 122.8, 122.4, 117.6, 83.2, 45.8, 28.0, 22.1.

(*S,E*)-*tert*-butyl 3-(1,3-diphenylallyl)-7-methoxy-1*H*-indole-1-carboxylate (**Boc-3n**): Colorless oil. 95% yield and 84% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 21.4$ min for (*S*)-isomer (major), $t_r = 49.0$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 7.5$ Hz, 2H), 7.32–7.26 (m, 7H), 7.25–7.21 (m, 2H), 7.07 (t, $J = 7.9$ Hz, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 6.80 (d, $J = 7.9$ Hz, 1H), 6.69 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 5.01 (d, $J = 7.4$ Hz, 1H), 3.93 (s, 3H), 1.62 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3) δ 150.0, 148.4, 142.2, 137.3, 132.8, 131.4, 131.3, 128.6, 127.4, 126.7, 126.5, 126.4, 125.2, 123.5, 122.4, 112.8, 106.9, 83.3, 55.8, 46.0, 28.1. HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_3$ [$\text{M} + \text{Na}$] $^+$: 462.2040, found 462.2043.

(*S,E*)-*tert*-butyl 7-chloro-3-(1,3-diphenylallyl)-1*H*-indole-1-carboxylate (**Boc-3o**): Colorless oil. 99% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 11.6$ min for (*S*)-isomer (major), $t_r = 17.3$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.36–7.27 (m, 10H), 7.26–7.21 (m, 3H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.67 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 5.00 (d, $J = 7.4$ Hz, 1H), 1.63 (s, 9H); ^{13}C -NMR

(125 MHz, CDCl₃) δ 149.1, 141.7, 137.0, 133.2, 132.7, 131.5, 130.8, 128.6, 128.5, 128.4, 127.4, 127.3, 126.8, 126.5, 126.4, 123.4, 122.4, 120.4, 118.7, 84.5, 45.8, 27.9. HRMS (ESI): calcd for C₂₈H₂₆CINNaO₂ [M + Na]⁺: 466.1544, found 466.1539.

(*S,E*)-*tert*-butyl 3-(1,3-di-*p*-tolylallyl)-1*H*-indole-1-carboxylate (**Boc-3p**) [19]: Colorless oil. 99% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 99:1 *v/v*, 0.5 mL/min, 25 °C, UV 254 nm), Retention times: t_r = 12.0 min for (*S*)-isomer (major), t_r = 14.1 min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.13 (brs, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.31–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.16–7.11 (m, 5H), 6.67 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.01 (d, *J* = 7.7 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 1.69 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.1, 139.4, 137.2, 136.3, 136.0, 134.7, 131.1, 130.6, 130.1, 129.4, 129.3, 128.5, 126.4, 124.5, 123.9, 123.5, 122.6, 120.4, 115.4, 83.8, 45.7, 28.4, 21.3.

(*S,E*)-*tert*-butyl 3-(1,3-bis(4-methoxyphenyl)allyl)-1*H*-indole-1-carboxylate (**Boc-3q**): Yellow oil. 85% yield and 90% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: t_r = 17.5 min for (*S*)-isomer (major), t_r = 19.3 min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.08 (s, 1H), 7.33–7.74 (m, 5H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.82 (t, *J* = 9.2 Hz, 4H), 6.51 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 4.95 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 6H), 1.65 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 159.1, 158.3, 150.0, 134.4, 130.4, 130.1, 130.0, 129.4, 127.5, 124.3, 123.7, 123.6, 122.4, 120.2, 115.3, 113.9, 83.7, 55.3, 55.2, 45.1, 28.3. HRMS (ESI): calcd for C₃₀H₃₁NNaO₄ [M + Na]⁺: 492.2145, found 492.2150.

(*S,E*)-*tert*-butyl 3-(1,3-bis(4-chlorophenyl)allyl)-1*H*-indole-1-carboxylate (**Boc-3r**) [19]: White solid (m.p. 65–67 °C). 99% yield and 95% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.7 mL/min, 25 °C, UV 254 nm), Retention times: t_r = 8.6 min for (*S*)-isomer (major), t_r = 11.7 min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 8.11 (brs, 1H), 7.36 (s, 1H), 7.32–7.23 (m, 10H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.64 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.01 (d, *J* = 7.2 Hz, 1H), 1.68 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.0, 140.5, 136.0, 135.6, 133.3, 132.8, 131.5, 130.7, 129.9, 129.7, 129.0, 128.9, 127.8, 124.7, 124.0, 122.7, 122.4, 120.1, 115.5, 84.1, 45.4, 28.4.

(*S,E*)-*tert*-butyl 3-(1,3-bis(4-nitrophenyl)allyl)-1*H*-indole-1-carboxylate (**Boc-3s**): Yellow oil. 87% yield and 97% ee, determined by chiral HPLC analysis (Chiralcel AD-H hexane/isopropanol, 93:7 *v/v*, 1.0 mL/min, 25 °C, UV 254 nm), Retention times: t_r = 43.5 min for (*R*)-isomer (minor), t_r = 54.4 min for (*S*)-isomer (major). ¹H-NMR (500 MHz, CDCl₃) δ 8.21–8.12 (m, 5H), 7.50 (d, *J* = 7.2 Hz, 4H), 7.42 (s, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24–7.14 (m, 2H), 6.85 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 1.68 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 148.7, 147.1, 142.9, 134.3, 130.7, 129.3, 129.0, 127.0, 124.9, 124.1, 122.8, 120.6, 119.5, 115.6, 84.3, 45.8, 28.2. HRMS (ESI): calcd for C₂₈H₂₅N₃NaO₆ [M + Na]⁺: 522.1636, found 522.1632.

3.4. General Procedure for the Pd-Catalyzed Asymmetric Allylic Etherification

Ligand **L1** (5.0 mg, 4 mol%) and [Pd(C₃H₅)Cl]₂ (2.2 mg, 2 mol%) were dissolved in DCM (1.0 mL) in a Schlenk tube under Ar. After 0.5 h of stirring at room temperature, allylic acetate **2a** (0.3 mmol) dissolved in DCM (0.5 mL) was added, followed by alcohol **4** (0.9 mmol) dissolved in DCM (0.5 mL) and Cs₂CO₃ (195 mg, 0.9 mmol). The mixture was stirred at 0 °C for 5 h and then was diluted with CH₂Cl₂ and washed with saturated NH₄Cl (aq). The organic layers were dried over MgSO₄ and filtered, and the solvents were evaporated in vacuo. The residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the corresponding product **5**.

(*S,E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (**5a**) [44]: Colorless oil. 99% yield and 98% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.5 mL/min, 25 °C, UV 254 nm), Retention times: t_r = 12.2 min for (*S*)-isomer (major), t_r = 13.4 min for (*R*)-isomer (minor). ¹H-NMR (500 MHz, CDCl₃) δ 7.46–7.30 (m, 14H), 7.27–7.23 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 15.9,

7.0 Hz, 1H), 5.04 (d, $J = 7.0$ Hz, 1H), 4.62–4.57 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 141.0, 138.2, 136.5, 131.4, 130.2, 129.6, 128.4, 128.3, 127.6, 127.4, 126.9, 126.5, 81.5, 70.0.

(*S,E*)-(3-((4-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (**5b**) [44]: Colorless oil. 97% yield and 97% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 v/v , 0.5 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 18.0$ min for (*S*)-isomer (major), $t_r = 23.8$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 4H), 7.32–7.29 (m, 5H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.36 (dd, $J = 15.9, 7.0$ Hz, 1H), 5.01 (d, $J = 7.0$ Hz, 1H), 4.51 (s, 2H), 3.82 (s, 3H); ^{13}C -NMR (125 MHz, CDCl_3) δ 159.1, 141.2, 136.6, 131.4, 130.4, 130.3, 129.3, 128.5, 127.6, 126.9, 126.5, 113.7, 81.2, 69.7, 55.2.

(*S,E*)-(3-((4-bromobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (**5c**) [44]: Colorless oil. 93% yield and 91% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 95:5 v/v , 0.5 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 10.2$ min for (*S*)-isomer (major), $t_r = 11.2$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.47 (d, $J = 8.3$ Hz, 2H), 7.42–7.36 (m, 6H), 7.31–7.27 (m, 3H), 7.25–7.23 (m, 3H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.32 (dd, $J = 15.9, 7.1$ Hz, 1H), 4.97 (d, $J = 7.1$ Hz, 1H), 4.55–4.48 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 140.9, 137.5, 136.5, 131.8, 131.5, 130.1, 129.4, 128.7, 128.6, 127.9, 127.0, 126.7, 121.4, 81.9, 69.4.

(*S,E*)-(3-((3-bromobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (**5d**) [45]: Colorless oil. 95% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 v/v , 0.5 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 14.3$ min for (*S*)-isomer (major), $t_r = 15.9$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.44–7.39 (m, 7H), 7.33–7.29 (m, 4H), 7.26–7.21 (m, 2H), 6.65 (d, $J = 15.9$ Hz, 1H), 6.36 (dd, $J = 15.9, 7.1$ Hz, 1H), 5.02 (d, $J = 7.0$ Hz, 1H), 4.58 (q, $J = 12.2$ Hz, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 140.9, 136.5, 131.8, 130.6, 130.0, 128.6, 127.9, 127.0, 126.7, 126.1, 122.6, 82.1, 69.4.

(*S,E*)-(3-((2-bromobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (**5e**) [46]: Colorless oil. 93% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OJ-H hexane/isopropanol, 99:1 v/v , 0.3 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 73.1$ min for (*S*)-isomer (major), $t_r = 81.9$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.69 (d, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.57–7.47 (m, 6H), 7.45–7.39 (m, 4H), 7.35–7.24 (m, 2H), 6.80 (d, $J = 15.9$ Hz, 1H), 6.47 (dd, $J = 15.9, 7.0$ Hz, 1H), 5.17 (d, $J = 7.1$ Hz, 1H), 4.76 (q, $J = 13.1$ Hz, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 141.0, 137.9, 136.6, 132.9, 132.5, 131.8, 130.0, 129.2, 128.9, 128.6, 127.8, 127.4, 126.9, 126.7, 82.4, 69.8.

(*S,E*)-2-(((1,3-diphenylallyl)oxy)methyl)naphthalene (**5f**) [40]: Colorless oil. 97% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 98:2 v/v , 1.0 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 7.3$ min for (*S*)-isomer (major), $t_r = 10.2$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 7.84–7.79 (m, 4H), 7.51–7.45 (m, 5H), 7.40–7.37 (m, 4H), 7.32–7.28 (m, 3H), 7.23 (t, $J = 7.3$ Hz, 1H), 6.66 (d, $J = 15.9$ Hz, 1H), 6.39 (dd, $J = 15.9, 7.0$ Hz, 1H), 5.06 (d, $J = 7.0$ Hz, 1H), 4.74 (s, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 141.2, 136.7, 136.0, 133.4, 133.1, 131.7, 130.3, 128.6, 128.2, 128.0, 127.8, 127.7, 127.1, 126.7, 126.5, 126.1, 125.9, 125.8, 81.7, 70.3.

(*S,E*)-2-(((1,3-diphenylallyl)oxy)methyl)pyridine (**5g**) [44]: Colorless oil. 86% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 v/v , 0.8 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 25.0$ min for (*S*)-isomer (major), $t_r = 36.8$ min for (*R*)-isomer (minor). ^1H -NMR (500 MHz, CDCl_3) δ 8.56 (d, $J = 4.6$ Hz, 1H), 7.74–7.71 (m, 1H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 4H), 7.32 (t, $J = 7.6$ Hz, 3H), 7.25 (t, $J = 7.3$ Hz, 1H), 7.21–7.19 (m, 1H), 6.72 (d, $J = 15.8$ Hz, 1H), 6.40 (dd, $J = 15.8, 7.1$ Hz, 1H), 5.11 (d, $J = 7.1$ Hz, 1H), 4.78 (dd, $J = 34.2, 13.5$ Hz, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 158.7, 148.9, 140.7, 136.4, 131.7, 129.8, 128.4, 127.7, 126.8, 126.5, 122.1, 121.2, 82.5, 71.1.

(*S,E*)-(3-ethoxyprop-1-ene-1,3-diyl)dibenzene (**5h**) [44]: Colorless oil. 98% yield and 99% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 v/v , 0.5 mL/min, 25 °C, UV 254 nm),

Retention times: $t_r = 9.2$ min for (*S*)-isomer (major), $t_r = 10.4$ min for (*R*)-isomer (minor). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.42–7.35 (m, 6H), 7.31–7.27 (m, 3H), 7.22 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.34 (dd, $J = 15.9, 7.1$ Hz, 1H), 4.93 (d, $J = 7.1$ Hz, 1H), 3.61–3.56 (m, 1H), 3.52–3.48 (m, 1H), 1.27 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 141.6, 136.7, 131.2, 130.7, 128.5, 127.7, 127.6, 126.9, 126.6, 82.6, 64.0, 15.4.

(*S,E*)-(3-(*but-3-en-1-yloxy*)prop-1-ene-1,3-diyl)dibenzene (**5i**) [44]: Colorless oil. 97% yield and 95% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99.2:0.8 *v/v*, 0.4 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 10.3$ min for (*S*)-isomer (major), $t_r = 12.1$ min for (*R*)-isomer (minor). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.40–7.34 (m, 6H), 7.30–7.26 (m, 3H), 7.22 (t, $J = 7.4$ Hz, 1H), 6.62 (d, $J = 15.9$ Hz, 1H), 6.31 (dd, $J = 15.9, 7.0$ Hz, 1H), 5.90–5.81 (m, 1H), 5.11–5.02 (m, 2H), 4.92 (d, $J = 7.0$ Hz, 1H), 3.60–3.56 (m, 1H), 3.50–3.46 (m, 1H), 2.43 (q, $J = 6.8$ Hz, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 141.4, 136.6, 135.3, 131.3, 130.5, 128.5, 127.7, 127.6, 126.8, 126.6, 116.3, 82.7, 68.0, 34.4.

(*S,E*)-2-((1,3-diphenylallyl)oxy)-2,3-dihydro-1H-indene (**5j**) [41]: Colorless oil. 96% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H hexane/isopropanol, 99:1 *v/v*, 0.5 mL/min, 25 °C, UV 254 nm), Retention times: $t_r = 13.7$ min for (*S*)-isomer (major), $t_r = 14.8$ min for (*R*)-isomer (minor). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.45–7.36 (m, 6H), 7.32–7.30 (m, 3H), 7.26–7.15 (m, 5H), 6.65 (d, $J = 15.9$ Hz, 1H), 6.37 (dd, $J = 15.9, 7.0$ Hz, 1H), 5.12 (d, $J = 6.9$ Hz, 1H), 4.55–4.51 (m, 1H), 3.25–3.02 (m, 4H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 141.4, 140.8, 136.5, 131.1, 130.6, 128.4, 127.5, 126.8, 126.5, 126.3, 124.5, 80.9, 77.9, 39.5.

4. Conclusions

SMI-PHOX ligand exhibited good catalytic performance in Pd-catalyzed asymmetric allylic alkylation reactions of indoles with 1,3-diaryl-2-propenyl acetate. The reactions afforded the corresponding products with high yields (up to 98%) and enantioselectivities (up to 98% ee) for a broad scope of indole derivatives. SMI-PHOX ligand was determined to be the most efficient P,N-ligand for this reaction. Furthermore, SMI-PHOX ligand was also efficient for Pd-catalyzed asymmetric allylic etherification with hard aliphatic alcohols as nucleophiles. Up to 99% yield and 99% ee were obtained. Further applications of these ligands in other asymmetric transformations are currently under development in our laboratory.

Supplementary Materials: The supplementary materials including NMR spectra and HPLC traces of the compounds are available online.

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Sample Availability: Samples of the compounds are available from the authors.



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